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New liquid crystalline di- and tetra-acrylates for network formation

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New liquid crystalline diacrylates and tetra-acrylates containing four to six aromatic rings were synthesized and characterized, and their mesophase behaviour was investigated. They are designed to be used in combination with chiral molecules to form cholesteric mesophases which can be crosslinked by photopolymerization. The acrylates presented exhibit broad mesophase ranges since mesogenic moieties longer than three are employed. Most diacrylates show no isotropization, due to premature thermal polymerization above 180°C. Additionally, liquid crystalline dipropionates were synthesized as reference compounds which cannot be crosslinked, and selected examples of these exhibit isotropization temperatures as high as 238°C prior to thermal degradation. Substituents at the mesogenic moiety have a great influence on the mesophase characteristics. Bulky substituents such as the *tert*-butyl group, induce a nematic mesophase, whereas compounds with small substituents (e.g. $^{-}OCH_3$) or unsubstituted molecules also exhibit smectic phases. Tetra-acrylates with unsubstituted and substituted mesogenic units feature nematic mesophases only as a result of the additional spacers attached. Here isotropization was observed without polymerization at temperatures around 120–160°C.

1. Introduction

In recent years liquid crystalline acrylates have attracted a great deal of interest. They can easily be oriented, e.g. by shear, and the orientation can be fixed by photopolymerization thus forming anisotropic, highly crosslinked networks. Due to the liquid crystalline nature of the monomers and their shear orientation, anisotropic mechanical, electrical, optical and also thermal properties are obtained [1–4]. In the presence of a chiral centre directly linked in the molecular structure or simply by addition of a chiral molecule (dopant), the mixture arranges in a helicoidal structure resulting in a cholesteric mesophase [5]. By photopolymerization, the pendant acrylate groups are crosslinked, the orientation is permanently fixed and a cholesteric network is obtained. These networks exhibit special optical properties, caused by the selective reflection of light and the angular dependence of the reflected wavelength resulting in the so-called 'colour flop' [6–8]. The materials are typically used for effect inks and pigments [9] or polarizers [10]. So far, diacrylates with mesogenic units of three or four aromatic rings have been employed for cholesteric mixtures [1, 11–14]. Another system investigated is based on nematic twin mesogen diacrylates [15, 16]. Furthermore, the acrylate functionality can be replaced by 1,5-hexadiene groups yielding photopolymerizable nematic liquid crystals [17].

In contrast to the liquid crystalline diacrylates possessing three aromatic rings at most, the mesophase can be broadened by the extension of the mesogenic unit to four and more aromatic rings. A broad nematic phase to start with is important, since the addition of the chiral dopant and/or reactive solvents will decrease the mesophase range of the final cholesteric mixture and hence the processing region. Such long and relatively stiff mesogenic units however suffer from high transition temperatures coupled with decreased solubity. Therefore this paper reports the properties of liquid crystalline acrylates featuring long rigid mesogenic units in combination with bulky or polar substituents, and non-coplanar moieties which will in return lower transition temperatures but enhance solubility in reactive solvents.

The present work investigates a series of liquid crystalline diacrylates, tetra-acrylates and dipropionates consisting of mesogenic units containing four to six aromatic rings. The mesophase behaviour of the diacrylates is studied and compared with the behaviour of the dipropionates,

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which represent reference compounds since they cannot be polymerized. The introduction of an additional two acrylate groups at the mesogenic unit will increase the density of a cholesteric network which might be advantageous for systems diluted by, for example, reactive solvents. Therefore the mesophase characteristics of the liquid crystalline tetra-acrylates are also examined.

The liquid crystalline compounds presented here exhibit a larger aspect ratio and therefore should be useful also for the preparation of lyotropic liquid crystalline systems. Based on the theory of Flory [18, 19], compounds featuring a large aspect ratio can be used for the preparation of lyotropic mesophases at a lower concentration, since the axial ratio is a function of the amount of solvent that can be added to a system of rod-like molecules yielding a lyotropic solution. Lyotropic systems can indeed be prepared with compounds presented here; the characterization of the lyotropic mixtures, their network formation and their cholesteric film properties are the topics of another publication [20].

2. Synthesis

This article describes the synthesis of calamitic liquid crystals functionalized with two or four acrylic groups, so enabling formation of highly crosslinked networks. In contrast to other systems investigated so far [1, 11, 13, 14], the objective of the synthetic efforts presented here is the design of mesogenic units consisting of four to six aromatic rings. As mentioned before, the mesophase can be broadened by such extensions of the mesogenic unit. An optimal broad mesophase range is characterized by a low crystal–nematic transition and isotropization at high temperatures, preferably after crosslinking occurs. For example, the structure of a tetra-acrylate with six aromatic rings synthesized in the course of this work is depicted in figure 1.

The target liquid crystalline compounds consist of a mesogenic core with three to six aromatic rings, a flexible C6 spacer unit and acrylate end-groups, enabling photocrosslinking. In addition non-polymerizable dipropionates were synthesized for comparison. The synthesis of the liquid crystalline systems is accomplished in three steps: (i) the synthesis of new diols, (ii) the design of the spacer unit with crosslinkable groups, and (iii) the combination of two spacer units with the diols. In this way, to the number of aromatic rings in the diol unit two more are added in the final condensation step. This synthetic strategy is outlined in greater detail in the following paragraphs. The numbering of the liquid crystalline compounds is based on the diols in table 1, completed by a suffix a for diacrylates, b for dipropionates and c for tetra-acrylates.

2.1. *Synthesis of diols*

All diols used for the synthesis of the liquid crystalline compounds are listed in table 1. Diols 1–3 are commercially available.

Diol 4 was synthesized according to a modified literature procedure [21, 22]. The mesogenic diols possessing three or more aromatic rings are accessible by two synthetic routes. The synthetic pathway depends on the substitution pattern at the aromatic rings. The mesogenic diols 5, 6, 7, 11 and 12, which are unsubstituted or have only small substituents at the aromatic core, could easily be synthesized via an azeotropic esterification reaction [17, 23] in *p*-xylene catalysed with *p*-toluenesulphonic acid. The synthesis is illustrated for 5–7 in scheme 1. This procedure is also suitable for scale-up and after purification 60–80% yields are obtained.

Diols featuring more bulky *tert*-butyl or phenyl groups as substituents are not accessible by the azeotropic esterification reaction. Probably due to steric hindrance, no complete conversion was achieved. Therefore the synthesis of diols **8–10** was accomplished via a protection group strategy which is outlined for 8 and 9 in scheme 2.

In the first step, the hydroxy group of the 4-hydroxybenzoic acid (**13**) or vanillic acid (**15**) was protected using benzyl chloroformate (**16**). The protected acid was then converted into the acid chloride by thionyl chloride. The protected acid chlorides **17** and **18** were reacted with *tert*-butylhydroquinone (**19**) using triethylamine as base. Finally deprotection was accomplished with hydrogen and palladium [24] as catalyst, giving the diols **8** and **9**.

2.2. *Synthesis of functionalized spacer units*

The spacer units were synthesized according to literature procedures [1, 25–27] in a three step procedure which

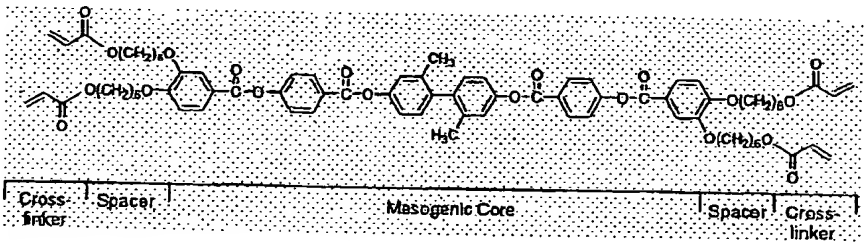
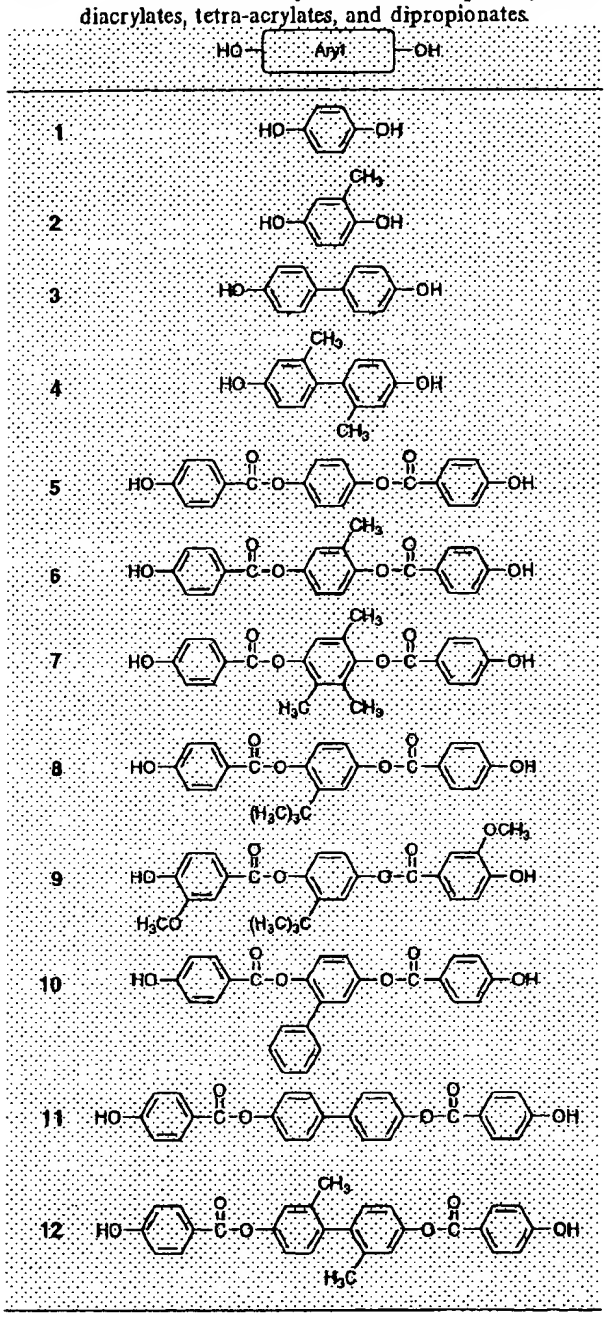
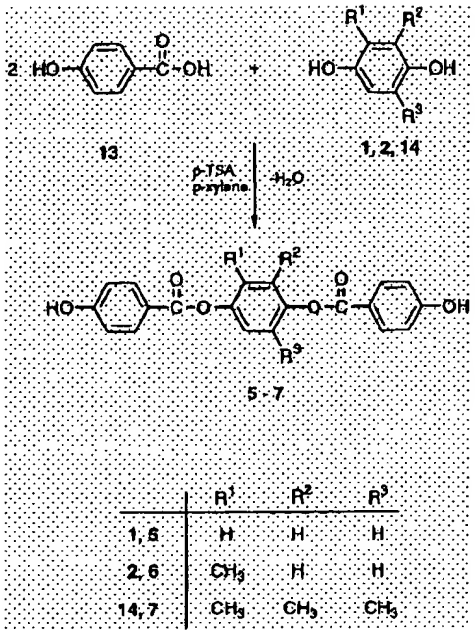


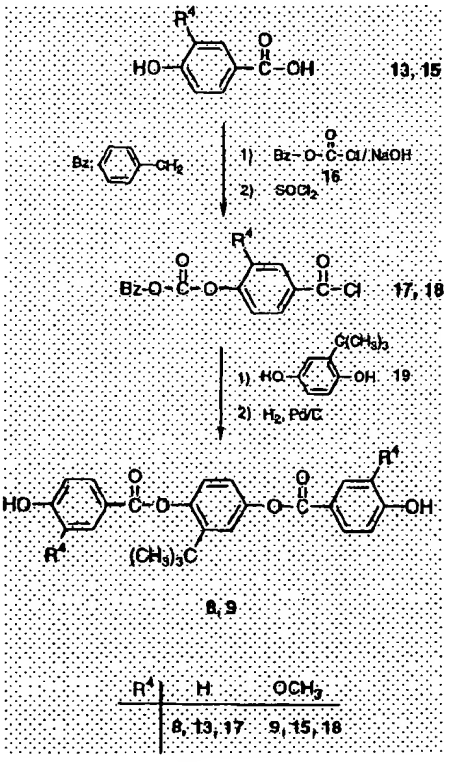
Figure 1. Example for a tetra-acrylate structure, consisting of a mesogenic core, symmetrically attached spacer, and crosslinker.

Table 1. Diols used for the synthesis of the liquid crystalline diacrylates, tetra-acrylates, and dipropionates.



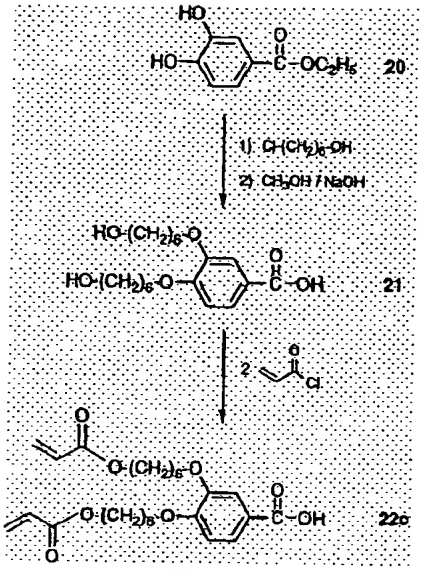


Scheme 1.



Scheme 2.

is shown in scheme 3 for **22c**. 6-Chlorohexanol, as the hydroxy-functionalized C6 spacer, is attached to the protected (esterified) hydroxy benzoic acid (**20**) in 2-butanone as solvent. Deprotection with potassium hydroxide in methanol yields **21**, and finally the acrylate moiety is introduced by condensation with acryloyl chloride. Hence, the synthesis of the di- and tetra-acrylates, indicated by the suffix **a** or **c**, respectively, is completely analogous except for the starting compounds. The non-polymerizable dipropionates (**b**) were synthesized in the same manner using propionyl chloride. Yields were in the range 50–80%.



Scheme 3.

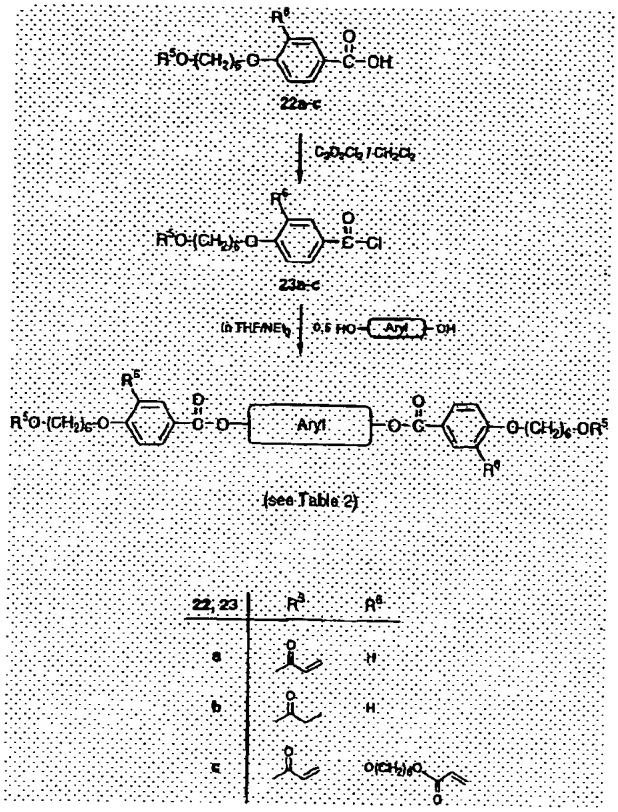
2.3. *Synthesis of liquid crystalline diacrylates, tetra-acrylates, and dipropionates*

Diacrylates **1a–3a** have been synthesized before, and the literature references are included in table 2. All other compounds were synthesized by coupling the diols **4–12** (see table 1) with a two-fold amount of the appropriate spacer unit as outlined in scheme 4. The acids **22a–c** were converted into the acid chlorides **23a–c** employing oxalyl chloride. These were condensed with the different diols forming the functionalized liquid crystalline compounds in yields in the range 40–80%, depending on the substituents in the diols. The mesogenic core of the resulting liquid crystalline compounds finally consists of the aromatic ring of the spacer units **22a–c** plus the aromatic rings of the diols. Hence, the longest mesogenic units synthesized in the course of this work are realized in **12a**, **11c**, and **12c** with six aromatic rings total. All liquid crystalline compounds and their most characteristic data are listed in table 2, other analytical data are included in the Experimental section.

3. Thermal characterization and mesophase behaviour

3.1. *Thermal stability of the diols 1–12*

All diols were examined by thermogravimetric analysis combined with simultaneous DSC measurements. Melting points were additionally determined by polarizing optical microscopy (POM) using a hot stage. All data are included in the Experimental section. Only the simple diols **1**, **2**, **4** and highly substituted diol **9** exhibit melting points, at 172, 127, 137 and 116°C, respectively. The other diols do not exhibit a melting point prior to thermal degradation. For diols **5–10** with three aromatic rings, decomposition starts between 276 and 294°C in a nitrogen



Scheme 4.

atmosphere. The most thermostable compound is **11** with commencement of degradation at 320°C, whereas the dimethyl substituted diol **12** starts to decompose at 242°C.

3.2. *Mesophase behaviour*

The mesophase behaviour of the liquid crystalline compounds was investigated by DSC, POM, and in some cases with temperature dependent SAXS. All results are summarized in table 2. To avoid thermal polymerization during the measurements, 2 wt% of sulphur was added as an inhibitor to diacrylates and tetra-acrylates.

3.2.1. *Diacrylates*

The mesophase behaviour of **1a–3a** is described in the literature [11, 14] and all three systems exhibit a clearing point in the range 111–151°C. All other compounds, except **4a** and **9a**, show no clearing point up to 175°C. Measurements above 175°C always lead to thermal polymerization despite the inhibitor. Compound **4a** exhibits a melting point at 81°C; above this temperature the compound shows a nematic mesophase which turns isotropic at 122°C. Diacrylate **3a**, as the non-methyl substituted analogue of **4a**, exhibits a melting point at

Table 2. Mesophase behaviour of all the liquid crystalline compounds investigated. Enthalpies (kJ mol^{-1}) in parentheses.

Compound	Diol (see table 1)	Thermal mesophase characterization/°C
Diacrylate		
1a	1	Cr 108 (SmC 88) N 155 I [11]
2a	2	Cr 86 N 116 I [11]
3a	3	Cr 83 SmX 107 SmC 111 I [14]
4a	4	Cr 81 (53.4) N 122 (2.00) I
5a	5	Cr 102 (41.0) (1st heating) X 146 (3.04) X 156 (14.1) SmA
6a	6	Cr 107 (19.0) X 115 (0.21) N
7a	7	Cr 125 (27.8) N
8a	8	Cr 109 (32.6) N
9a	9	g 7 (0.15)[a] N 148 (2.48) I, 1st heating: Cr 112 (53.9) N 148 I
10a	10	Cr 91 (21.2) N
12a	12	Cr 129 (42.6) N
Dipropionate		
1b	1	Cr 118 (77.3) (SmC 96) N 149 (0.83) I SmC: 34.8 Å (90°C)[b] T_{dec} = 260[c]
5b	5	Cr 108 (40.9) X 137 (1.40) X 161 (16.6) SmA 204 (2.00) N SmA: 33.5 Å (170°C) T_{dec} = 330
6b	6	Cr 119 (31.2) SmA 125 (0.98) N; SmA: 32.7 Å (115°C) T_{dec} = 330
8b	8	Cr 103 (31.2) N 238 (3.11) I T_{dec} = 300
Tetra-acrylate		
5c	5	Cr 121 (79.6) N 127 (0.61) I
6c	6	Cr 107 (58.0) N 122 (0.79) I
11c	11	Cr 123 (77.0) N 155 (3.88) I
12c	12	Cr 132 (52.0) N 143[d] I

[a] Δc_p in kJ K^{-1} mol^{-1}.
[b] Small angle X-ray characterization at the temperature specified.
[c] Onset of the decomposition temperature determined at 10 K min^{-1}.
[d] Detectable only on cooling or by polarization microscopy.

83°C, a highly ordered phase SmX and a SmC phase above 107°C; the clearing point is at 111°C [14]. The introduction of the two methyl groups in **4a** simplifies the mesophase behaviour, since now only a nematic phase is observed. This pronounced influence of the substituents on the mesophase behaviour is also evident for the diacrylates with five aromatic rings, **5a**, **6a** and **8a**; this influence is demonstrated with the help of the DSC runs, see figure 2.

Compound **5a**, which is unsubstituted at the mesogenic unit, has a melting point at 102°C, but this is only visible during the first heating run. In the range up to 175°C two additional transitions at 146 and 156°C were determined, as depicted in figure 2. The mesophase above 156°C was identified by X-ray measurements as a SmA phase with a *d*-spacing of 33.0 Å. The two other mesophases in the range 102–156°C (marked with X in table 2 and figure 2) are probably mesophases of higher order.

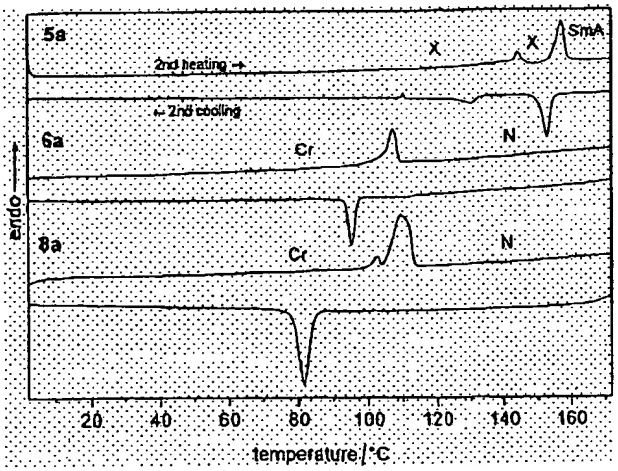


Figure 2. DSC curves of diacrylates **5a**, **6a** and **8a** (2nd heating and 2nd cooling; heating rate 10 K min^{-1} with 2 wt % sulphur as inhibitor).

These mesophases were not identified in detail since their nature is not important for the final application of the acrylates as components in cholesteric mixtures. Compound **6a** contains one methyl group at the inner aromatic ring and exhibits a transition into a nematic phase at 115°C. Compound **7a**, substituted with three methyl groups at the inner aromatic ring, is characterized by a melting point into a nematic phase at 125°C. The *tert*-butyl substituted diacrylate **8a** exhibits a melting transition into a nematic mesophase at 109°C. In **10a**, with a pendant phenyl group, this transition is further lowered to 91°C. For **9a**, which consists of a mesogenic unit of five aromatic rings that are substituted with a *tert*-butyl and two methoxy groups, crystallization is suppressed on first cooling; in the second heating run at the glass transition of 7°C a nematic glass is formed. Compound **9a** is the only diacrylate with five aromatic rings showing an isotropization transition (at 148°C); this process is usually impeded by thermal polymerization. Thus, the mesophase behaviour of the diacrylates in this series is simplified by the introduction of more bulky substituents or more than one substituent in the mesogenic core. The only diacrylate synthesized with six aromatic rings, **12a**, exhibits a crystalline–nematic transition at 129°C.

3.2.2. *Dipropionates*

The liquid crystalline dipropionates **1b**, **5b**, **6b** and **8b** were synthesized as reference compounds. The mesophase behaviour of these materials, in particular their isotropization, can be examined until thermal decomposition sets in. **1b** was prepared for comparison with diacrylate **1a**, which is well-known in the literature [1, 11]. **1a**, with a mesogenic unit of three aromatic rings, has a melting point of 108°C, giving then a nematic mesophase up to the isotropization temperature at 155°C. Furthermore, on cooling a monotropic SmC phase with a transition temperature of 88°C is observed. **1b**, possessing the same mesogenic unit, melts at 118°C to form a nematic mesophase which becomes isotropic at 149°C. On cooling, a monotropic SmC phase is formed below 96°C with a d-spacing of 34.8 Å. Thermal decomposition of **1b** in a nitrogen atmosphere starts at 260°C. Now comparing the mesophase behaviours of **1a** and **1b**, the same kinds of mesophase occur, but the phase transition temperatures are shifted resulting in a narrower liquid crystalline region for **1b**.

The liquid crystalline behaviours of **5b**, **6b** and **8b**, containing a mesogenic unit of five aromatic rings, are compared with those of the corresponding diacrylates **5a**, **6a**, **8a**. As mentioned before, the diacrylates suffered from thermal polymerization at temperatures above 175°C, but the dipropionates could be examined up to their decomposition temperatures. Thermal decomposition of the unsubstituted **5b** and the methyl substituted **6b** starts at 330°C, and the *tert*-butyl substituted **8b** is thermally stable up to 300°C. **5b** melts at 108°C, exhibits an additional phase transition between ordered X phases at 137°C, and forms a SmA phase at 161°C; then at 204°C a nematic phase is formed. A phase transition into the isotropic state could not be detected up to 300°C. Figure 3 shows a polarizing photomicrograph of **5b** at 150°C in the higher temperature of the two X phases for which the textures in the polarizing microscope are similar; a mosaic texture and arcs can be observed.

The mesophases of dipropionate **5b** were examined by temperature dependent X-ray measurements starting in the nematic phase at 220°C. The diffractograms of the different mesophases are shown in figure 4.

Cooling to 170°C reveals an additional 1 0 0 peak indicating, with support from microscopy observations, a SmA phase with a d-spacing of 33.5 Å. At lower temperatures additional peaks are observed suggesting the presence of other highly ordered phases; however these were not characterized further.

Compound **6a** melts at 119°C to a SmA phase followed by a transition into a nematic phase at 125°C. A transition into the isotropic state could not be observed up to 300°C. The SmA phase of **6b** was also examined by X-ray, and a d-spacing of 32.7 Å was calculated. The *tert*-butyl substituted dipropionate **8b** melts at 103°C to form only a nematic mesophase which turns isotropic at 238°C; **8b** is the only dipropionate with a mesogenic unit of five aromatic rings that exhibits an isotropization transition prior to thermal decomposition. In this case a broad nematic phase of about 130°C was observed.

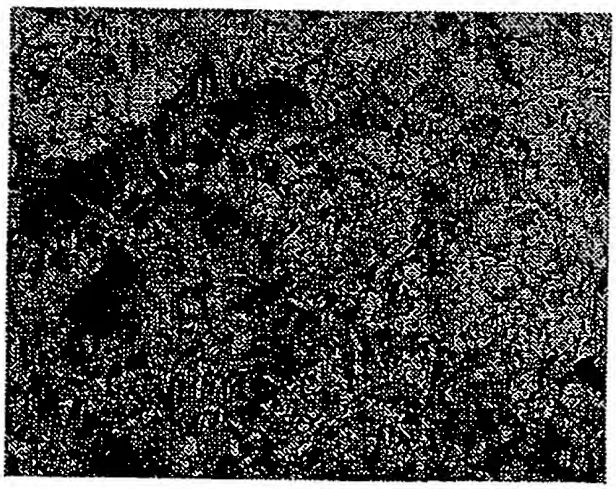


Figure 3. Polarizing photomicrograph of dipropionate **5b** (T = 150°C; magnification 1 : 200).

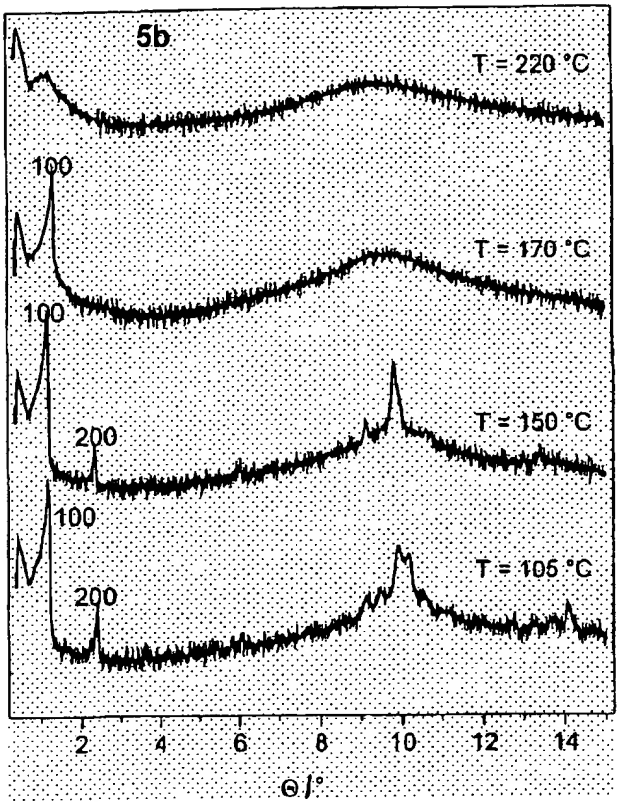


Figure 4. Temperature dependent X-ray diffractogram of dipropionate **5b** showing the formation of the SmA (d-spacing: 33.5 Å) phase at 170°C.

With increasing size of the substituents at the mesogenic unit, the phase behaviour of the dipropionates is simplified and the transition into the nematic phase is shifted to lower temperatures. Comparing the mesophase behaviours of **5a**, **6a** and **8a** with **5b**, **6b** and **8b** it can be concluded that diacrylates and dipropionates with the same substituent at the mesogenic unit behave very similarly; the transition temperatures are shifted relative to one another, but not in any systematic way.

3.2.3. *Tetra-acrylates*

The mesophase behaviours of tetra-acrylates **5c**, **6c**, **11c** and **12c** were investigated in the same manner; their DSC curves are shown in figures 5(*a*) and 5(*b*).

All tetra-acrylates studied exhibit a nematic mesophase after melting. The unsubstituted compound **5c**, having five aromatic rings in the mesogenic unit, melts at 121°C followed by isotropization at 127°C. The inset in figure 5(*a*) magnifies the nematic region of **5c** and the corresponding transition for the heating and cooling curves. Compound **6c** melts at 107°C and the transition into the isotropic state is at 122°C. Two tetra-acrylates **11c** and **12c**, featuring six aromatic rings, were also examined. **11c** which has no substituent has a melting point at 123°C followed by the nematic–isotropic transition at 155°C. In **12c** the biphenyl unit is not coplanar due to substitution by two methyl groups. This compound melts at 132°C and at 143°C isotropization is observed. The phase transitions of **5c**, **6c** and **11c** could be determined by DSC measurements without problems. However, in the 2nd heating run of **12c** the nematic phase is not observed, but it is detectable in the cooling run, figure 5(*b*), and by POM.

Comparing the mesophase behaviour of the tetra-acrylates and diacrylates, the two additional spacer units induce on the one hand smaller range mesophases, but on the other hand simplify the mesophase behaviour, as only nematic mesophases are observed, followed in all cases by isotropization at relatively low temperatures in the range 122–155°C.

4. Conclusions

The synthesis and mesophase characterization of liquid crystalline acrylates with up to six aromatic rings in the mesogenic unit is described. These materials are designed for the development of cholesteric mixtures which can be processed into pigment particles. Besides a variety of diacrylates, tetra-acrylates were synthesized permitting a higher crosslink density. To investigate the possible phase behaviour of diacrylates at higher temperatures, dipropionates as non-polymerizable reference compounds were also synthesized and investigated.

Liquid crystalline diacrylates with long mesogenic units consisting of three aromatic rings exhibit mesophases with a range of around 40°C. However, on increasing the number of aromatic rings, and depending on the substituents at the mesogenic unit, the mesophase range is further broadend and no transition into the isotropic state can be detected before thermal polymerization. As these materials exhibit broad mesophases and a high axial ratio, they seem good candidates to form lyotropic nematic and cholesteric liquid crystalline systems.

Liquid crystalline dipropionates possessing the same mesogenic core as the corresponding diacrylates, exhibit a similar mesophase behaviour to the diacrylates. With bulky substituents at the mesogenic unit, the dipropionates exhibit a clearing point, whereas small substituents or the unsubstituted compounds exhibit no clearing point due to thermal degradation. However, the lack of thermal polymerization permitted mesophase characterization by X-ray scattering at elevated temperatures and the d-spacings of the smectic phases were determined.

Liquid crystalline tetra-acrylates with mesogenic units of five or six aromatic rings exhibit only nematic mesophase behaviour. The mesophase behaviour is influenced

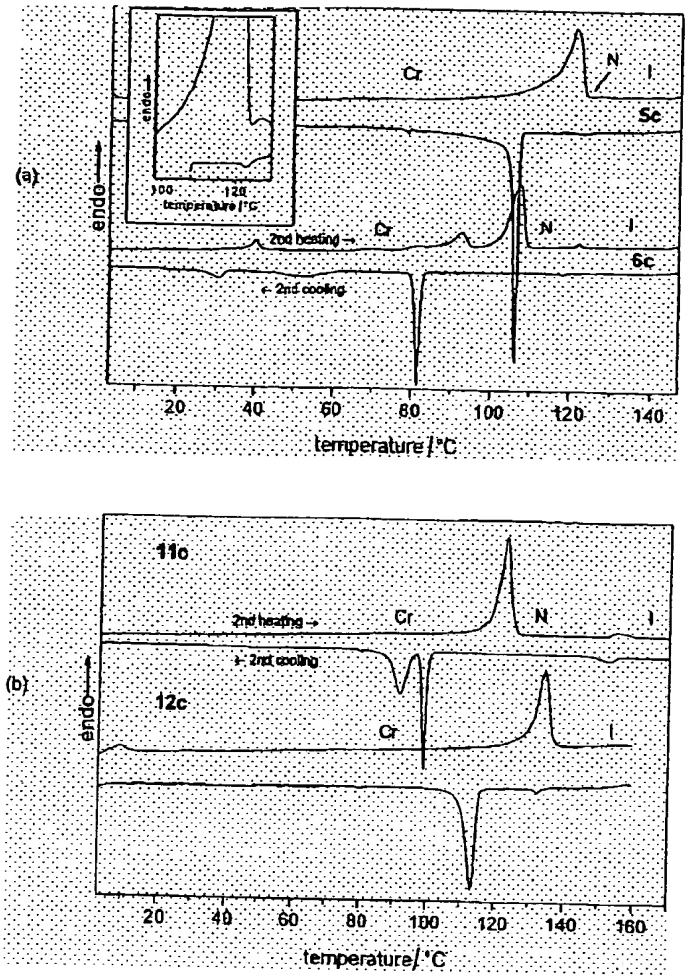


Figure 5. DSC curves of tetra-acrylates 5c and 6c (*a*), and 11c and 12c (*b*). The inset in (*a*) magnifies the narrow nematic range of 5c. (2nd heating and 2nd cooling, heating rate 10 K min^{-1} with 2 wt % sulphur as inhibitor).

by the two additional spacers and the acrylate units, as indicated by a smaller mesophase ranges and lower transition temperatures compared with the diacrylates.

5. Experimental

5.1. *Characterization*

The mesophase behaviour was studied using a Perkin Elmer DSC 7 (at 10 K min^{-1}) and a Nikon Diaphot 300 polarizing microscope with a Mettler FP 82 hot stage. For DSC investigations of acrylic compounds, polymerization was inhibited with 2 wt % sulphur. Small angle X-ray investigations (SAXS) were carried out with a Huber Guinier Goniometer 600 with a Huber Quartz Monochromator 611, using $CuK_{\alpha'}$ radiation and a screen system, beam catcher and oven developed at the University of Bayreuth. Thermal stabilities and selected melting points were determined with a Netzsch STA 409 simultaneous TGA/DSC apparatus using a nitrogen atmosphere (75 ml min^{-1}) and heating rates of 10 K min^{-1}. FTIR spectra were measured with a Bio-Rad Digilab FTS-40; IR vibrations of the compounds synthesized [28] are not very characteristic and are therefore omitted in this article. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker AC 250. CHN-elemental analysis results for new compounds were found to be satisfactory in all cases in relation to the proposed structures.

5.2. *Materials*

5.2.1. *Chemicals*

Tetrahydrofuran (THF) and 1,4-dioxan were heated under reflux over potassium and distilled. Methylene chloride was heated over calcium hydride and distilled. Acryoyl chloride was distilled twice and stabilized with 2,6-bis(*t*-butyl)-*p*-cresol (BHT). 2,2′-Dimethyl-4,4′-dihydroxybiphenyl (*4*) was synthesized according to [21, 22] in 60% yield. 4-(6-Hydroxyhexyloxy)benzoic acid, 4-(6-acryloyloxyhexyloxy)benzoic acid (**22a**) and 4-(6-propanoyloxyhexyloxy)benzoic acid (**22b**) were synthesized according to literature procedures [1, 25, 26]. All other chemicals were commercially available and used as received.

5.2.2. *General procedure for the preparation of compounds 5, 6, 7, 11 and 12* (scheme 1, table 1)

8.29 g (60 mmol) of 4-hydroxybenzoic acid (**13**) and 0.03 mol of the corresponding aromatic diol, 0.42 g (3 mmol) of *p*-toluene sulphonic acid and 150 ml of *p*-xylene were placed in a flask equipped with a Dean–Stark trap. The reaction mixture was heated at reflux for 24 h, when the crude product was filtered off and purified as specified below. The melting point was determined by the onset of the DSC melting peak. Also listed are ^{1}H NMR data obtained in DMSO-d_6.

5: 81% (m.p. 294°C), washing with ethanol. δ (ppm): 10.54 (s, 2H), 8.00 (d, 4H), 7.31 (s, 4H), 6.94 (d, 4H). **6**: 85% (m.p. 276°C), washing with diethyl ether. δ (ppm): 10.53 (s, 2H), 8.00 (t, 4H), 7.17 (m, 3H), 6.94 (dd, 4H), 2.15 (s, 3H). **7**: 57%, (m.p. 298°C), recrystallization from methanol. δ (ppm): 10.54 (s, 2H), 8.01 (t, 4H), 6.98 (s, 1H), 6.94 (dd, 4H), 2.06 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H). **11**: 77%, (m.p. 320°C), recrystallization from cyclohexanone. δ (ppm): 10.52 (s, 2H), 8.00 (d, 4H), 7.74 (d, 4H), 7.32 (d, 4H), 6.93 (d, 4H). **12**: 74%, (m.p. 242°C), recrystallization from dioxane. δ (ppm): 10.52 (s, 2H), 7.99 (d, 4H), 7.15 (m, 6H), 6.93 (d, 4H), 2.04 (s, 6H).

5.2.3. *Diols 8–10* (scheme 2, table 1)

0.143 mol of **13** or **15** was dissolved in 300 ml of aq. NaOH (1M) and 29.6 g (0.173 mol) of benzyl chloroformate (**16**) were added slowly at 0°C. The reaction mixture was stirred for 2 h and poured into 500 ml of aq. HCl (2M); the precipitate was filtered off and recrystallized from acetone/water. The acid chloride was made by dissolving 0.13 mol of the protected hydroxybenzoic acid in 150 ml of 1,2-dichloroethane; 12 ml (0.17 mol) of thionyl chloride was then added and the solution heated at reflux for 2 h. The solvent and excess of thionyl chloride were removed by distillation. The crude acid chloride **17** or **18** was dissolved in 100 ml of 1,2-dichloroethane and added to a mixture of 9.72 g (0.06 mol) of **19**, 37 ml (0.26 mol) of triethylamine and 100 ml of 1,2-dichloroethane. For **10**, phenylhydroquinone was used instead of **19**. The reaction mixture was heated at reflux for 2 h, cooled to room temperature, filtered, and the 1,2-dichloroethane removed under vacuum. The residue was dissolved in chloroform, washed with water, the organic phase dried with Na_2SO_4, the solvent removed by rotatory evaporation and the crude product recrystallized from cyclohexane (R = H and **10**) or reprecipitated from a THF solution into ice water (R = $^-$OCH$_3$). Finally the benzyl formate group was removed by adding 0.033 mol of the protected mesogenic diol and 2.5 g of palladium (5%) on activated charcoal to 200 ml of THF. The reaction mixture was saturated continuously with hydrogen and stirred at 40°C for 12 h. After filtration the solvent was partly removed and the diols precipitated into ice water.

8: 89% (dec. 288°C). ^{1}H NMR (DMSO) δ (ppm): 10.54 (s, 2H), 8.00 (dd, 4H), 7.19 (d, 2H), 6.94, (t, 5H), 1.30 (s, 9H). **9**: 63% (m.p. 116°C). ^{1}H NMR (CDCl$_3$) δ (ppm): 7.85 (m, 2H), 7.70 (dd, 1H), 7.13 (m, 4 H), 6.17, (d, 2H), 3.99 (s, 6H), 1.39 (s, 9H). **10**: 54% (dec. 290°C). ^{1}H NMR (CDCl$_3$) δ (ppm): 8.24 (dd, 2H), 8.04 (dd, 2H), 7.34 (m, 23H), 5.29 (s, 2H), 5.27 (s, 2H).

5.2.4. *3,4-Di-[6-hydroxyhexyloxy)]benzoic acid (21)* (scheme 3)

10.93 g (0.06 mol) of 3,4-dihydroxybenzoic acetate (**20**), 5.3 g (0.133 mol) of NaOH, 19.9 g (0.133 mol) of NaI and 17.74 ml (0.133 mol) of 6-chlorohexanol were added to 200 ml of 2-butanone. After stirring for 20 h at 60°C, the 2-butanone was removed under vacuum. The residue was dissolved in 300 ml of aq. NaOH (0.4M) and shaken with 400 ml diethyl ether. The organic layer was separated and the solvent removed by distillation; the residue was dissolved in 200 ml of methanol, and after adding 60 ml of aq. KOH (4.5M) the mixture was heated under reflux for 20 h. Methanol was removed by distillation and the residue dissolved in 200 ml of aq. NaOH (0.4M). The solution was washed with 100 ml of diethyl ether and the aqueous phase acidified with conc. aq. HCl. The precipitate of **21** was collected and recrystallized from water.

21: 67% (m.p. 133–135°C). ^{1}H NMR (DMSO) δ (ppm): 12.59 (s, 1H), 7.51 (dd, 1H), 7.41 (d, 1H), 7.01 (d, 1H), 4.33 (s, 2H), 3.97 (m, 4H), 3.40 (m, 4H), 1.71 (m, 4H), 1.38 (m, 12H).

5.2.5. *3,4-Di-(6-acryloyloxyhexyloxy)benzoic acid (22c)*

13.6 g (0.04 mol) of 3,4-di-(6-hydroxyhexyloxy)benzoic acid (**21**), 9.6 ml (0.06 mol) of *N,N*-diethylaniline and 100 mg of BHT (inhibitor) were added to 150 ml of 1,4-dioxan and heated to 60°C. 6.9 ml (0.085 mol) of acryloyl chloride were added slowly and the mixture was stirred at 60°C for 2.5 h. After cooling to room temperature, the mixture was poured into stirred ice water, and the crude product filtered and recrystallized from isopropanol.

22c: 71% (no melting prior to polymerization). ^{1}H NMR (DMSO) δ (ppm): 12.55 (s, 1H), 7.51 (dd, 1H), 7.51 (dd, 1H), 7.41 (d, 1H), 7.01 (d, 1H), 6.29 (dd, 2H), 6.14 (dd, 2H), 5.90 (dd, 2H), 4.03 (m, 8H), 1.72 (m, 4H), 1.61 (m, 4H), 1.41 (m, 8H).

5.2.6. *Synthesis of the diacrylates (a), dipropionates (b) and tetra-acrylates (c)* (scheme 4, table 2)

15 mmol of the required substituted benzoic acid **22a–c** was dispersed in 40 ml of methylene chloride and cooled with ice. An 8–10 molar excess of oxalyl chloride

(12 ml or 0.15 mol) was added slowly. The reaction mixture was stirred at room temperature until no further gas generation was observed. Methylene chloride and the excess of oxalyl chloride were removed by distillation in vacuum. The remaining acid chloride was dried under high vacuum at room temperature.

7 mmol of diols **1–12**, 3.5 ml (25 mmol) of triethylamine and 100 mg of BHT were added to 100 ml of THF. The appropriate acid chloride **22a–c** was also dissolved in THF and slowly added, maintaining the temperature at 0°C, and the mixture stirred for 24 h at room temperature. Triethylamine hydrochloride was removed by filtration and the THF under vacuum. The residue was dissolved in chloroform, shaken with water and the organic phase removed by distillation; the crude product was purified by recrystallization (solvent) or column chromatography (solvent mixture). All ^{1}H NMR spectra were recorded in $CDCl_3$.

4a: 54% (ethanol). δ (ppm): 8.14 (d, 4H), 7.12 (m, 6H), 6.96 (d, 4H), 6.39 (dd, 2H), 6.10 (dd), 5.80 (dd, 2H), 4.17 (t, 4H), 4.04 (t, 4H), 2.09 (s, 6H), 1.83 (m, 4H), 1.72 (m, 4H), 1.49 (m, 8H). DSC: Cr 81 N 122 I (2nd heating, 2 wt % sulphur). **5a**: 60% (first toluene, then chloroform/ethyl acetate 40/1). δ (ppm): 8.30 (d, 4H), 8.15 (d, 4H), 7.40 (d, 4H), 7.30 (s, 4H), 6.95 (d, 4H), 6.40 (dd, 2H), 6.10 (dd, 2H), 5.80 (dd, 2H), 4.20 (t, 4H), 4.05 (t, 4H), 1.85 (m, 4H), 1.72 (m, 4H), 1.50 (m, 8H). DSC: Cr 102 (1st heating only) X 146 X 156 SmA (2nd heating, 2 wt % sulphur), X-ray: *d*-spacing SmA = 33.0 Å (T = 165°C). **6a**: 56% (first toluene, then cyclohexane/ethyl acetate 2/1). δ (ppm): 8.27 (m, 4H), 8.14 (d, 4H), 7.36 (dd, 4H), 7.17 (m, 3H), 6.97 (d, 4H), 6.39 (dd, 2H), 6.10 (dd, 2H), 5.80 (dd, 2H), 4.14 (t, 4H), 4.05 (t, 4H), 2.26 (s, 3H), 1.85 (m, 4H), 1.73 (m, 4H), 1.51 (m, 8H). DSC: Cr 107 X 115 N (2nd heating, 2 wt % sulphur). **7a**: 60% (isopropanol). δ (ppm): 8.30 (m, 4H), 8.14 (d, 4H), 7.36 (m, 4H), 6.97 (m, 5H,), 6.39 (dd, 2H), 6.11 (dd, 2H), 5.80 (dd, 2H), 4.17 (t, 4H), 4.04 (t, 4H), 2.18 (s, 3H), 2.13 (s, 6H), 1.84 (m, 4H), 1.71 (m, 4H), 1.50 (m, 8H). DSC: Cr 125 N (2nd heating, 2 wt % sulphur). **8a**: 79% (isopropanol). δ (ppm): 8.30 (m, 4H), 8.14 (d, 4H), 7.37 (m, 4H), 7.26 (d, 1H), 7.14 (s, 2H), 6.97 (d, 4H), 6.40 (dd, 2H), 6.11 (dd, 2H), 5.80 (dd, 2H), 4.17 (t, 4H), 4.05 (t, 4H), 1.82 (m, 4H), 1.70 (m, 4H), 1.52 (m, 8H), 1.38 (s, 9H). DSC: Cr 109 N (2nd heating, 2 wt % sulphur). **9a**: 59% (cyclohexane/ethyl acetate 2/1). δ (ppm): 8.10 (d, 4H), 7.82 (m, 4H), 7.16 (m, 3H), 7.10 (s, 2H), 6.91 (d, 4H), 6.34 (dd, 2H), 6.05 (dd, 2H), 5.75 (dd, 2H), 4.12 (t, 4H), 3.99 (t, 4H), 3.84 (s, 6H), 1.78 (m, 4H), 1.66 (m, 4H), 1.44 (m, 8H), 1.34 (s, 9H). DSC: g 7 N 148 I (2nd heating, 2 wt % sulphur). **10a**: 47% (isopropanol). δ (ppm): 8.32 (d, 2H), 8.16 (m, 6H), 7.40 (m, 12H), 7.00 (d, 4H), 6.44 (dd, 2H), 6.14 (dd, 2H, 5.84 (dd, 2H), 4.20 (t, 4H), 4.05 (t, 4H), 1.86 (m, 4H), 1.75 (m, 4H), 1.51 (m, 8H). DSC: Cr 91 N (2nd heating, 2 wt % sulphur). **12a**: 57% (cyclohexane/ethyl acetate 2/1). δ (ppm): 8.28 (d, 4H), 8.15 (d, 4H), 7.36 (d, 4H), 7.14 (m, 6H), 6.97 (d, 4H), 6.39 (dd, 2H), 6.11 (dd, 2H), 5.81 (dd, 2H), 4.17 (t, 4H), 4.05 (t, 4H), 2.11 (s, 6H), 1.84 (m, 4H), 1.72 (m, 4H), 1.49 (m, 8H). DSC: Cr 129 N (2nd heating, 2 wt % sulphur).

1b: 80% (isopropanol). δ (ppm): 8.14 (d, 4H), 7.25 (s, 4H), 6.97 (d, 4H), 4.07 (m, 8H), 2.33 (q, 4H), 1.84 (m, 4H), 1.68 (m, 4H), 1.49 (m, 8H), 1.14 (t, 6H). DSC: Cr 118 (SmC 96) N 149 I (2nd heating). X-ray: *d*-spacing SmC = 34.8 Å (T = 90°C). **5b**: 69% (toluene). δ (ppm): 8.27 (d, 4H), 8.15 (d, 4H), 7.37 (d, 4H), 7.30 (s, 4H), 6.97 (d, 4H), 4.05 (m, 8H), 2.32 (q, 4H), 1.84 (m, 4H), 1.67 (m, 4H), 1.48 (m, 8H), 1.13 (t, 6H). DSC: Cr 108 X 137 X 161 SmA 204 N (2nd heating). X-ray: *d*-spacing SmA = 33.5 Å (T = 170°C). **6b**: 70% (toluene). δ (ppm): 8.27 (m, 4H), 8.14 (d, 4H), 7.36 (dd, 4H), 7.15 (m, 3H), 6.97 (d, 4H), 4.07 (m, 8H), 2.31 (m, 7H), 1.83 (m, 4H), 1.67 (m, 4H), 1.48 (m, 8H), 1.13 (t, 6H). DSC: Cr 119 SmA 125 N (2nd heating). X-ray: *d*-spacing SmA = 32.7 Å (T = 115°C). **8b**: 66% (isopropanol). δ (ppm): 8.28 (m, 4H), 8.15 (d, 4H), 7.37 (m, 4H), 7.26 (m, 1H), 7.14 (s, 2H), 6.97 (d, 4H), 4.05 (m, 8H), 2.31 (q, 4H), 1.83 (m, 4H), 1.67 (m, 4H), 1.47 (m, 8H), 1.39 (s, 9H), 1.13 (t, 6H). DSC: Cr 103 N 238 I (2nd heating).

5c: 43% (chloroform/ethyl acetate 40/1). δ (ppm): 8.23 (d, 4H), 7.78 (dd, 2H), 7.60 (d, 2H), 7.31 (d, 2H), 7.19 (s, 4H), 6.88 (d, 4H), 6.34 (dd, 4H), 6.06 (dd, 4H), 5.75 (dd, 4H), 4.08 (m, 16H), 1.84 (m, 8H), 1.66 (m, 8H), 1.45 (m, 16H). DSC: Cr 121 N 127 I (2nd heating, 2 wt % sulphur). **6c**: 68% (chloroform/ethyl acetate 40/1). δ (ppm): 8.29 (m, 4H), 7.84 (dd, 2H), 7.67 (d, 2H), 7.38 (d, 3H), 7.20 (m, 4H), 6.95 (d, 2H), 6.40 (dd, 4H), 6.12 (dd, 4H), 5.81 (dd, 4H), 4.14 (m, 16H), 2.28 (s, 3H), 1.88 (m, 8H), 1.72 (m, 8H), 1.52 (m, 16H). DSC: Cr 107 N 122 I (2nd heating, 2 wt % sulphur). **11c**: 72% (chloroform/ethyl acetate 40/1). δ (ppm): 8.31 (d, 4H), 7.84 (dd, 2H), 7.66 (m, 6H), 7.36 (m, 6H), 6.94 (d, 4H), 6.40 (dd, 4H), 6.12 (dd, 4H), 5.81 (dd, 4H), 4.15 (m, 16H), 1.90 (m, 8H), 1.73 (m, 8H), 1.52 (m, 16H). DSC: Cr 123 N 155 I (2nd heating, 2 wt % sulphur). **12c**: 42% (chloroform/ethyl acetate 40/1). δ (ppm): 8.31 (d, 4H), 7.85 (dd, 2H), 7.67 (d, 2H), 7.38 (d, 4H), 7.16 (m, 6H), 6.95 (d, 2H), 6.40 (dd, 4H), 6.12 (dd, 4H), 5.83 (dd, 4H), 4.13 (m, 16H), 2.13 (s, 6H), 1.91 (m, 8H), 1.73 (m, 8H), 1.50 (m, 16H). Hot stage/polarizing microscope: Cr 132 N 143 I.

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References

[1] Broer, D. J., Boven, J., Mol, G. N., and Challa, G., 1989, *Makromol. Chem.*, **190**, 2255.
[2] Jahromi, S., Lub, J., and Mol, G. N., 1994, *Polymer*, **35**, 622.
[3] Kelly, S. M., 1995, *J. mater. Chem.*, **5**, 2047.
[4] Kelly, S. M., 1998, *Liq. Cryst.*, **24**, 71.
[5] Broer, D. J., and Heynderickx, I., 1990, *Macromolecules*, **23**, 2474.
[6] Hikmet, R. A. M., Lub, J., and Broer, D. J., 1991, *Adv. Mater.*, **3**, 393.
[7] Lub, J., Broer, D. J., Hikmet, R. A. M., and Nierop, K. G. J., 1995, *Liq. Cryst.*, **18**, 319.
[8] Stohr, A., and Strohriegl, P., 1997, *J. macromol. Sci.—pure appl. Chem.*, **A34**, 1125.
[9] Meyer, F., 1998, *Farbe u. Lack*, **104**, 28.
[10] Broer, D. J., Lub, J., and Mol, G. N., 1995, *Nature*, **378**, 467.
[11] Broer, D. J., Hikmet, R. A. M., and Challa, G., 1989, *Makromol. Chem.*, **190**, 3201.
[12] Geibel, K., Hammerschmidt, A., and Strohmer, F., 1993, *Adv. Mater.*, **5**, 107.
[13] Rajaram, C. V., Hudson, S. D., and Chien, L. C., 1996, *Chem. Mater.*, **8**, 2451.
[14] Chien, L.-C., Boyden, M. N., Walz, A. J., and Citano, C. M., 1996, *Amer. chem. Soc. Symp. Ser.*, **632**, 182.
[15] Kürschner, K., and Strohriegl, P., 1999, *Mol. Cryst. liq. Cryst.*, **332**, 2727.
[16] Kürschner, K., and Strohriegl, P., 2000, *Liq. Cryst.*, **27**, 1595.
[17] Pfeuffer, T., Kürschner, K., and Strohriegl, P., 1999, *Macromol. Chem. Phys.*, **200**, 2480.
[18] Flory, P. J., 1956, *Proc. roy. Soc.*, **A234**, 60.
[19] Flory, P. J., 1984, *Adv. polym. Sci.*, **59**, 2.
[20] Schmitt, G., Giesa, R., and Schmidt, H.-W., *Adv. Materials* (in preparation).
[21] Percec, V., Zhao, M., Bae, J. Y., and Hill, D. H., 1996, *Macromolecules*, **29**, 3727.
[22] Grasser, W., Giesa, R., and Schmidt, H.-W., 2001, *Polymer*, **42**, 8529.
[23] Schuhmacher, P., Meyer, F., Etzbach, K.-H., and Siemensmeyer,K., 1997, German Patent DE 197 16 822 A1.
[24] Galli, G., Chiellini, E., Laus, M., and Angeloni, A. S., 1989, *Polym. Bull.*, **21**, 563.
[25] Portugall, M., Ringsdorf, H., and Zentel, R., 1982, *Makromol. Chem.*, **183**, 2311.
[26] Klemm, D., Schnabelrauch, M., Stein, A., Niemann, M., and Ritter, H., 1990, *Makromol. Chem.*, **191**, 2985.
[27] Stohr, A., 1998, PhD thesis, University of Bayreuth, Germany.
[28] Schmitt, G., 2000, PhD thesis, University of Bayreuth, Germany.